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ScienceDirect
Renewable and Sustainable Energy Reviews
11 (2007) 964–975
RENEWABLE & SUSTAINABLE ENERGY REVIEWS
www.elsevier.com/locate/rser

Thermoanalytical characterization of castor oil biodiesel

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Abstract

The castor oil seed has 47–49% of oil. Biodiesel obtained from castor oil has a lower cost compared to the ones obtained from other oils, as due its solvability in alcohol transesterification occurs without heating. The use of biodiesel will allow a reduction on the consumption of petroleum-derived fuels minimizing the harmful effects on the environment. This work wants to provide a thermoanalytical and physical-chemistry characterization of castor oil and biodiesel. Biodiesel was obtained with methyl alcohol and characterized through several techniques. Gas chromatography indicated methyl ester content of 97.7%. The volatilization of biodiesel starts and finishes under inferior temperatures than the beginning and final volatilization temperatures of castor oil. Biodiesel data are very close to the volatilization temperatures of conventional diesel.

Keywords: Biodiesel; Thermal analysis; Castor oil

Contents

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1364-0321/$ - see front matter
doi:10.1016/j.rser.2005.10.001

1. Introduction

Among the several possibilities considered in the literature, glycerides or vegetable oils constitute the most promising renewable source in order to obtain liquid fuels capable of substituting diesel oil. Besides its high calorific power, vegetable oils have qualities which distinguish them as sustainable fuels: the lack of sulfur in its chemical composition, the fact that its industrial production does not generate harmful substances to the environment and, also, the fact that they are made of vegetable cultivations that consume carbon dioxide during photosynthesis [1–3].

Castor oil is a triglyceride derived from ricinoleic acid, which is constituted of 90% of fatty acids present in the molecule and of 10% non-hydroxylated fatty acids, mainly by oleic and linoleic acids. Due to this particular chemical composition castor oil becomes highly valuable for industrial proposes [4,5].

When the transesterified oils (which receive the generic denomination of biodiesel) are processed to constitute alcohol esters, they can be used in diesel engines without need of any modification.

Biodiesel is an oxygenated fuel; therefore, it has a more complete firing, which allows reducing the engine pollutant emission. When there is a biodiesel/diesel blend, the more the percentage of biodiesel present in the blend, the bigger the reduction of that pollutant emission [6,7].

The engine performance with either the pure biodiesel or with the biodiesel/diesel blend is virtually the same, as the one obtained from pure diesel. In addition, biodiesel calorific power is closer to the diesel oil's and, even when it is added in small quantities, biodiesel provides a reasonable improvement on the fuel's lubricity. This characteristic is particularly important when the goal is to use a low-sulfured diesel, which has an admittedly low lubricity [8–10].

The possibilities of using the biodiesel are even more attractive in the most distant places, where the transportation cost is increased for petroleum-derived fuels. In addition, biodiesel is non-toxic and biodegradable which makes it an excellent fuel to be used in ecologically sensitive places such as lakes, national parks, estuaries, etc. [11,12].

In the last few decades thermal analysis tools such as thermogravimetry, differential scanning calorimetry, differential thermal analysis, etc. have become more important. The data obtained from these techniques can provide useful information in terms of reaction mechanism, kinetic parameters, thermal stability, phase transformation, heat of reaction, etc.

Through a complete knowledge of the properties that determine the identity patterns and biodiesel quality it will be possible to establish control parameters that will guarantee the quality of the product to be used in the energetic national matrix.

This work studied the thermoanalytical and physical-chemistry characterization of castor oil and biodiesel using some techniques such as thermal analysis and gas chromatography (GC).

2. Experimental

Castor oil was converted into biodiesel through the alkaline transesterification reaction. Methanol was added in the 20% ratio in mass and also 1% of the potassium hydroxide catalyst dissolved in alcohol. Then the mixture was shaken in ambient temperature for 30 min. Glycerin was removed after the decantation process which has taken 30 min and then biodiesel was purified, presenting a 98% yield.

Transesterification, which is also called alcoholysis, consists in the substitution of the radical of one esther by the radical of one alcohol in a process like hydrolysis, except for the fact of using one alcohol instead of water. The transesterification reaction is represented by the general equation

$$\mathrm{RCOOR'} + \mathrm{R''OH} \leftrightarrow \mathrm{RCOOR''} + \mathrm{R'OH}. \quad (1)$$

If methanol is used in the reaction above, it will be called methanolysis and if the chosen alcohol is ethanol, the reaction will be called ethanolysis. We call biodiesel the methyl or ethyl esters of fatty acids obtained from this reaction.

A primordial step to obtain the transesterification reaction is the control of the formation reaction of the potassium hydroxide catalyst. The anion hydroxide electron attacks the hydrogen of hydroxyl of methanol, breaking the O–H linking, producing water and anion methoxide. The methoxide is the catalyst responsible for the production of linear esters (biodiesel). In excess, its electron attacks molecules of the vegetable oil, dislocating the glycerin. Together, hydroxyl in balance and the methoxide compete with each other, forcing an undesirable reaction of saponification.

Decree 255 of the Petroleum National Agency (ANP) supplies the preliminary specification of the Biodiesel B100, where its characteristics are determined by means of the norms of the Brazilian Association of Technical Norms (ABNT) and of the American Society for Testing and Materials (ASTM).

The density analyses were accomplished in a DA110 Kyoto Electronics densimeter. The kinematic viscosity analyses were accomplished in a TVB445 ISL viscometer. The color analyses were obtained in Koehler colorimeter, model Lico 100. Copper corrosion was obtained in Herzog equipment. Flash point was obtained from HFP380 Herzog equipment. The analyses for the sulfur content determination were performed in EDX 800 Shimadzu X-ray fluorescence sulfur analyzer. The samples were analyzed by GC in a Varian 3800 Chromatograph with a flame ionization detector, the 5% phenyl 95% polydimethylsiloxane column has dimensions $30\,\mathrm{m} \times 0.25\,\mathrm{mm}$. The temperatures of the injector and detector were set at 290 and 300 °C, respectively.

The thermogravimetric (TG) and calorimetric (DSC) curves were obtained in a SDT 2960 TA Instruments Simultaneous Thermobalance, in air atmosphere with a flow of 100 mL/min, using the dynamic method of analysis, at heating rates of 10, 15 and 20 °C/min and interval of temperature of 28–900 °C.

The determination of the calorific capacity of the oil and castor oil biodiesel was carried through from the data obtained for DSC, considering the calculations based on the execution of the program described below:

The calorific capacity of the sample (C_S), the calorific capacity of the reference material (C_r) and the heating rate are related through

$$C_S - C_r = \left(\frac{T_S - T_r}{\alpha R}\right), \quad (2)$$

where T_S = temperature of the sample in the steady state, T_r = temperature of the reference material, R = thermal resistance between the sample, material of reference and oven.

At this rate, $(T_S - T_r)$ is proportional to the difference in the calorific capacity of the sample and the material of reference. Hence, if the displacement of the DSC is S and the protection constant is k, the following expression can be written:

$$C_S - C_r = kS. \quad (3)$$

In the determination of the calorific capacity we use the following conditions:

- measured with the container of the empty sample (white),
- measure of the reference material (α-alumina),
- measure of the calorific capacity of the unknown sample, mass m_0, in grams, the container of the sample.

C_S^h and C_r^h are the calorific capacities of the support of the sample and the support of the reference material, respectively, and, c_0 and c, the specific heats of the material of reference and the sample, respectively, the following relations can be obtained:

$$(C_S^h - C_r^h) = kS_1, \quad (4)$$

$$(C_S^h - m_0 c_0) - C_r^h = kS_2, \quad (5)$$

$$(C_S^h - mc) - C_r^h = kS_3, \quad (6)$$

where S_1, S_2 and S_3 are, respectively, the thermal displacements of the DSC referring to the white, reference and sample.

Working with the Eqs. (4)–(6) we obtain the expression

$$\frac{mc}{m_0 c_0} = \frac{S_3 - S_1}{S_2 - S_1}. \quad (7)$$

Thus, the specific heat of the oil and biodiesel are given by

$$c = \frac{m_0 c_0}{m} \frac{S_3 - S_1}{S_2 - S_1}. \quad (8)$$

3. Results and discussion

3.1. Physical-chemistry characterization

The qualitative and quantitative composition in fatty acid of the castor oil is illustrated in Table 1. The castor oil possesses comparative atypical chemical characteristics to the majority of vegetable oils; therefore, it presents the ricinoleic acid trygliceride (12-hydroxy-9-octadecenoic), which is a less frequent hydroxylated fatty acid in vegetable oils, as its main constituent.

The accented presence of a unique type of fatty acid in the composition of the triglycerides is an outstanding characteristic of the castor oil. Ricinoleic acid which possesses 18 carbons, presents the peculiarity of being one of the few natural fatty acids whose chemical structure possesses three highly reactive functional groups: the carbonyl group in 1st carbon, the double linking or insaturation in 9th carbon and the hydroxyl group in 12th carbon. The functional groups present in the ricinoleic acid make it possible for the castor oil to be submitted to diverse chemical processes in which different products can be obtained, thence its vast industrial application.

After the process of attainment of biodiesel, as demanded by Decree 255 of the ANP, the physical-chemistry analyses were performed to identify and qualify biodiesel.

The data of GC indicated methyl ester content of 97.7%. The analyses of viscosity, sulfur, density, color, copper corrosion and flash point were performed according to

Table 1
Composition in fatty acid of castor oil

Fatty acid	Composition (%)
Ricinoleic acid	90.2
Linoleic acid	4.4
Oleic acid	2.8
Estearic acid	0.9
Palmitic acid	0.7
Dihidroxiestearic acid	0.5
Licosanoic acid	0.3
Linolenic acid	0.2

Table 2
Physical-chemistry properties of diesel, castor oil and biodiesel

Analyses	Castor oil	Biodiesel	Diesel
Viscosity (mm^2/s)	239.39	13.75	3.2
Sulfur (%)	0	0.0001	0.20
Density 15 °C (g/cm^3)	0.9573	0.9279	0.8503
Density 20 °C (g/cm^3)	0.9584	0.9245	0.8465
ASTM color	Yellow	Yellow	Red
Flash point (°C)	310	120	37
Copper corrosion	1	1	1

ASTM norms (Table 2). The presence of a bigger content of hydroxyacid in the castor oil is reflected in its coligative properties, such as high values of viscosity and density.

The high viscosity of the oil reduces the fuel atomization and increases fuel spray penetration. The bigger fuel spray penetration is considered to be partially responsible for the difficulties with deposits in the engine and thickening of the oil. However, these effects can be eliminated through the transesterification of the oil to form esthers. The transesterification process removes glycerin of the triglycerides and substitutes with radicals of the alcohol used for the conversion process. This process diminishes viscosity, but it keeps the cetane number.

Castor oil biodiesel presents bigger flash point and viscosity than mineral diesel type D. The bigger flash point of biodiesel guarantees greater security in the handling and storage. The biggest viscosity of biodiesel can be corrected through the use of blends, which present diesel norm values.

3.2. Thermal study

The study of the experimental factors that can influence the TG and calorimetric curves were performed with the objective of choosing the best experimental conditions to perform the analyses.

3.2.1. Influence of the heating rate

The dependence of the TG profile of the samples on heating rate was verified varying its heating rate using 10, 15 and 20 °C/min.

It was observed that, the higher the used heating rate, the higher the temperature to initiate and finish the process of thermal decomposition, as it can be observed in the Figs. 1–4. Hence, the heating rate that reproduces better results is 10 °C/min, but on increasing the heating rate to 15 and 20 °C/min reproduction of results becomes less effective.

Increasing the heating rate the distribution of the heat in the sample will be lower and the degradation process will be delayed. Thus, the sample will need higher temperatures to distribute the heat equally and to reach its temperature of degradation leading to a displacement of the TG curve to higher temperatures and displacement of the calorimetric curves temperatures peak.

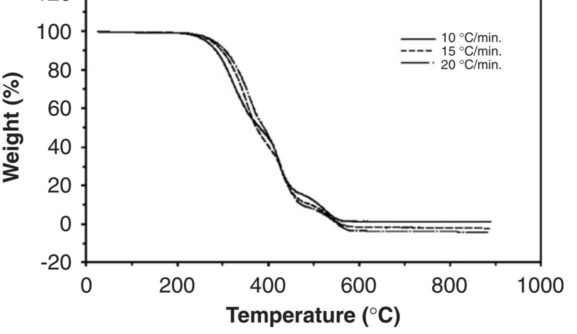


Fig. 1. TG curves of castor oil at different heating rates.

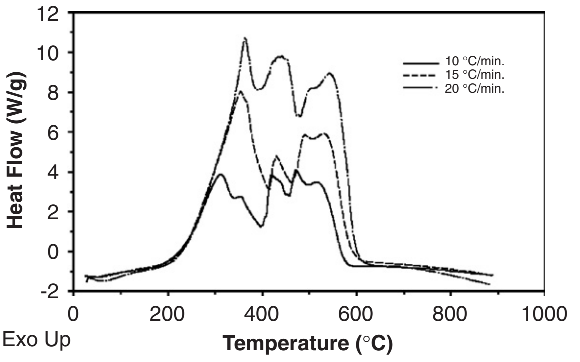


Fig. 2. DSC curves of castor oil at different heating rates.

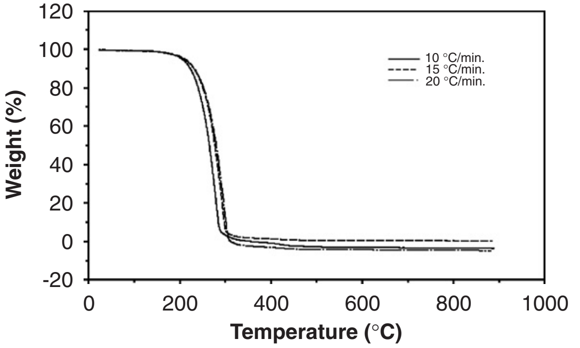


Fig. 3. TG curves of castor oil biodiesel at different heating rates.

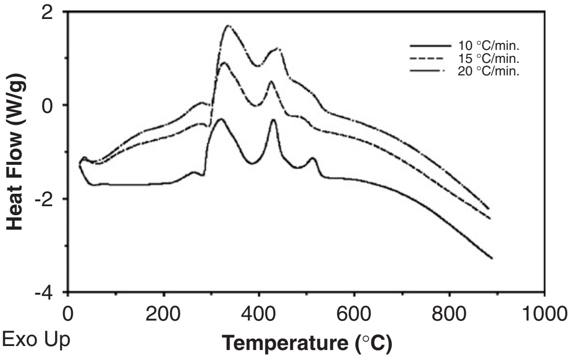


Fig. 4. DSC curves of castor oil biodiesel at different heating rates.

3.2.2. Influence of the atmosphere

The dependence of the TG profile of the samples as a function of atmosphere of the oven was verified at the heating rate 10 °C/min, varying the atmosphere, as synthetic air and nitrogen (Figs. 5–8).

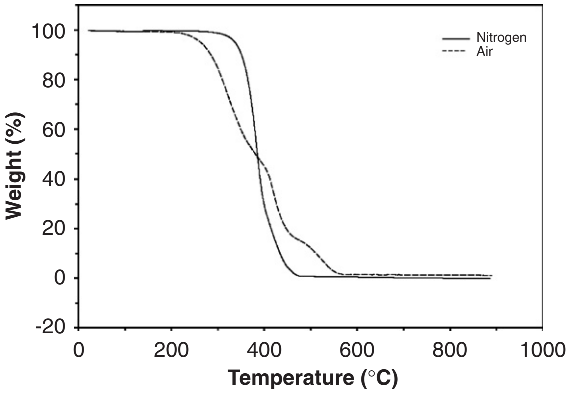


Fig. 5. TG curves of castor oil at different atmospheres.

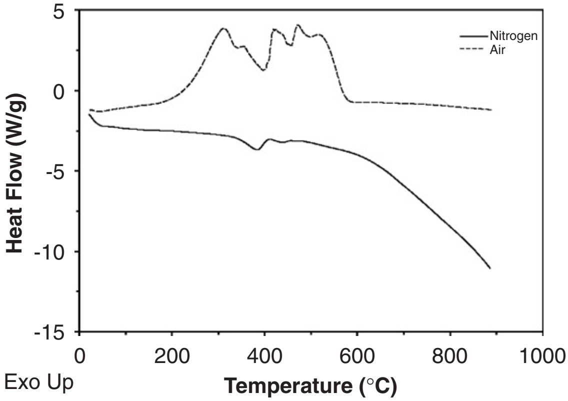


Fig. 6. DSC curves of castor oil at different atmospheres.

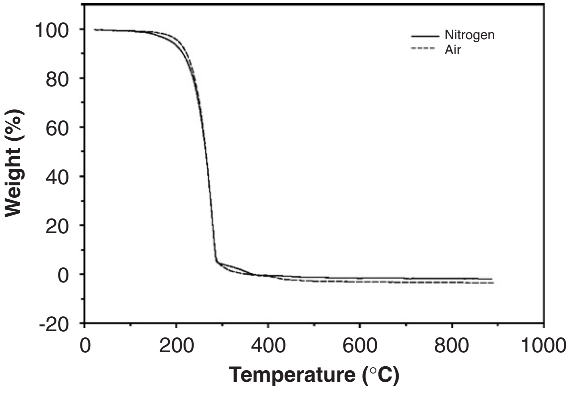


Fig. 7. TG curves of castor oil biodiesel at different atmospheres.

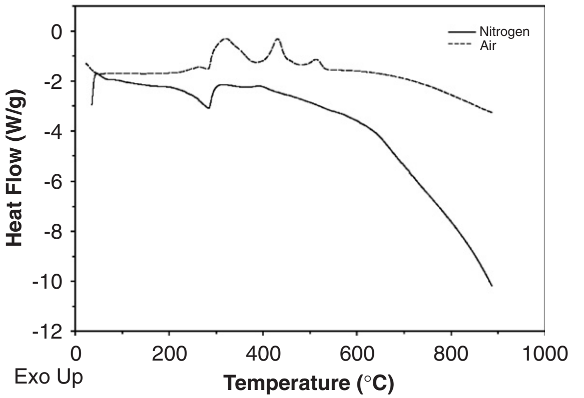


Fig. 8. DSC curves of castor oil biodiesel at different atmospheres.

The TG curve of a sample can liberate gaseous substances or react with one of the components of the atmosphere that involves it in the interior of the oven. If there is release of gaseous substance, the dissociation of the sample initiates as soon as its dissociation pressure equals the gas or vapor partial pressure in its immediate neighborhood. If the pressure of the gas increases, the speed of the reaction will diminish. However, the convection streams in the interior of the oven provoke a continuous renewal of the atmosphere of the sample, and this is one of the reasons for the curves of the samples, in different TG systems, not to be exactly the same.

The alteration of the oven atmosphere modified the TG profile indicating a larger number of stages of decomposition in the oxidant atmosphere, as in the calorimetric curves that had still presented inversion in the transitions. Therefore, in the inert nitrogen atmosphere the transitions had also been endothermic and in the synthetic air atmosphere the transitions had been exothermic.

So we define the heating rate of 10 °C/min as the best conditions for the analysis and synthetic air atmosphere, to prevent displacement of the TG and calorimetric profiles, to accomplish the study of the oxidation process that is a very important factor to define the useful lifetime and storage condition.

3.2.3. Thermogravimetric and calorimetric profile

Thermogravimetry and calorimetry had been used with the objective to analyze the thermal behavior of the castor oil and biodiesel, and thus to verify its TG and calorimetric profiles.

The TG curve of the castor oil presented three stages of thermal decomposition, which are consecutive and had been attributed to the volatilization and/or decomposition of the oil, mainly of ricinoleic fatty acid, at temperatures 196–390, 390–470 and 470–577 °C with respective mass losses 51%, 31% and 14%. The calorimetric curve of the castor oil presented three exothermic transitions attributed to the volatilization and/or decomposition process of the oil at temperatures 309, 419 and 531 °C presenting respective enthalpies 1967, 333 and 1128 J/g.

The TG curve of castor oil biodiesel presented two stages of thermal decomposition attributed to volatilization and/or decomposition of methyl esters at temperatures 150–334 and 334–513 °C with respective mass losses 97% and 3%. The calorimetric curve of castor

oil biodiesel presented four exothermic transitions attributed to the process of decomposition of esters at temperatures 259, 317, 431 and 516 °C presenting respective enthalpies 22, 359, 179 and 43 J/g.

The process of volatilization of castor oil biodiesel initiates and finishes in temperatures inferior to the castor oil volatilization beginning and end temperatures, coming close to the volatilization of conventional diesel temperatures. Hence, castor oil biodiesel potential is confirmed as a fuel alternative.

3.2.4. Calorific capacity

The knowledge of the calorific capacity (C_p) of biodiesel is of great practical importance in the engineering branch. Therefore, it is associated with the operations of refinery and other correlated processes. In the development of the equipment, the knowledge of the values of the calorific capacity, in some intervals of temperature, is fundamentally important, because these data can help to establish the conditions of operation under low temperatures. The calorific capacity can be used to evaluate other basic thermodynamic properties of fuels.

Table 3
Calorific capacity (C_p) of castor oil.

Temperature (°C)	C_p (J/g/K)
52.6	2.718
64.6	2.736
76.6	2.652
88.6	2.403
100.6	2.562
112.6	2.665
124.6	2.680

Table 4
Calorific capacity (C_p) of castor oil biodiesel.

Temperature (°C)	C_p (J/g/K)
55.4	1.855
60.4	1.964
65.4	1.988
70.4	1.876
75.4	2.044
80.4	2.029
85.4	2.047
90.4	2.135
95.4	2.215
100.4	2.143
105.4	2.203
110.4	2.225
115.4	2.259
120.4	2.362
125.4	2.179

The molar calorific capacities standard in the liquid phase (castor oil and biodiesel) had been determined according to the method described in the methodology. For the analyzed samples, the values of the specific heat had not varied substantially with temperature (Tables 3 and 4).

The calorific capacity of castor oil and biodiesel in the interval of 55–125 °C was 2.718–2.680 and 1.855–2.179 J/g K, respectively. It was verified that the castor oil presented a higher capacity of transference of heat compared to biodiesels'. However, many properties show no advantage in the use of vegetable oil in natura in diesel engines, as, for example, the high viscosity can cause clogging in the fuel system.

4. Conclusions

The presence of a higher content of hydroxyacids in the castor oil reflects its coligatives properties, such as viscosity and density. Castor oil biodiesel has lower cost compared to the one obtained from other vegetable oils due to its solubility in alcohol and thus the transesterification reaction can occur under the ambient temperature. Moreover, it does not contain sulfur, it has greater cetane number, which indicates a better quality of ignition, and it has more oxygen, making its combustion more complete.

The transesterification process diminished the viscosity of biodiesel and kept the cetane number. The flash point of biodiesel is greater than the diesel's one. Thus, biodiesel offers a better storage security, handling and use compared to conventional diesel.

The data of GC indicated a methyl ester content of 97.7%. The physical-chemistry characteristics of biodiesel had been determined to evaluate its capacity as fuel. Castor oil biodiesel presents combustion heat comparable to conventional diesel and high viscosity. Biodiesel attains ANP specifications, so it can be applied as fuel. Moreover, it will reduce the consumption of petroleum derivatives, will generate jobs and income in the northeastern region and will minimize the environment harmful effects.

The best conditions of TG and calorimetric analysis are heating rate of 10 °C/min and atmosphere of synthetic air, to prevent displacement of the TG and calorimetric profiles, as carried out in the study of the oxidation process.

The castor oil biodiesel has a great potential to be used in large scale as fuel for diesel engines. The ease of its use, mainly due to the fact of not needing substantial alterations in the engine, makes it an alternative fuel.

The benefits that can be obtained with the reduction of the use of petroleum derivative fuel had been placed in evidence. It has distinguishing possibility to reduce CO_2 production of fossil origin in the sector of transports. In this way, it becomes easier to take care of the determinations of the Kyoto Protocol.

Acknowledgements

The authors acknowledge CNPq and ANP for the financial support.

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